Unexpected Gas Sorption Displayed by Organic Clathrates

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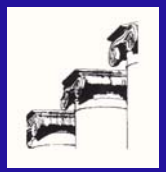

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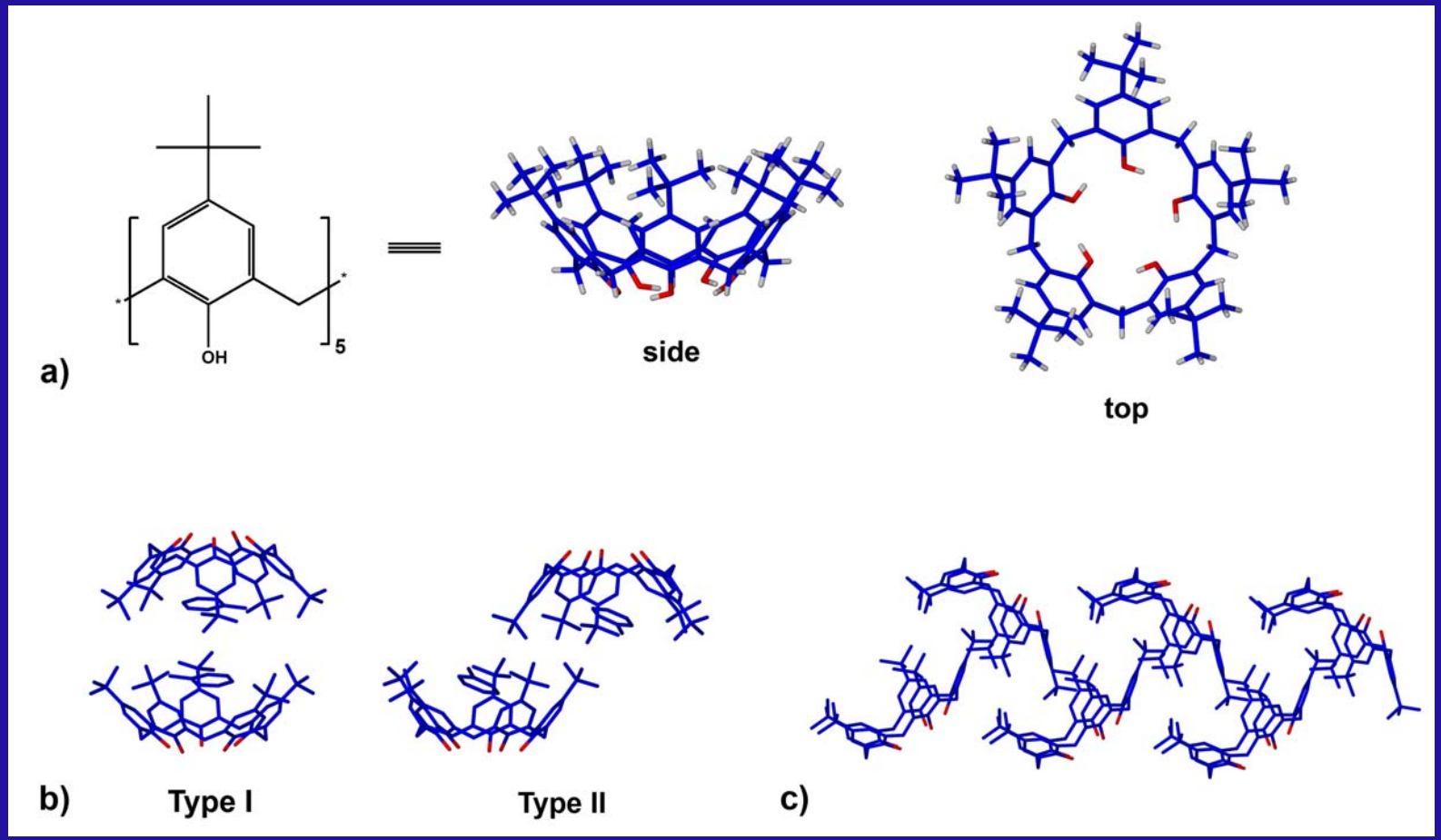
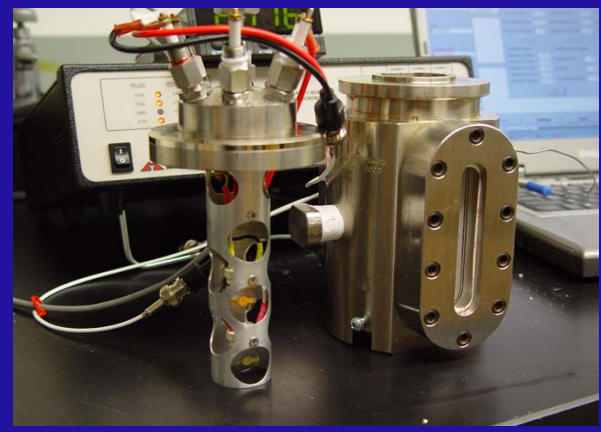
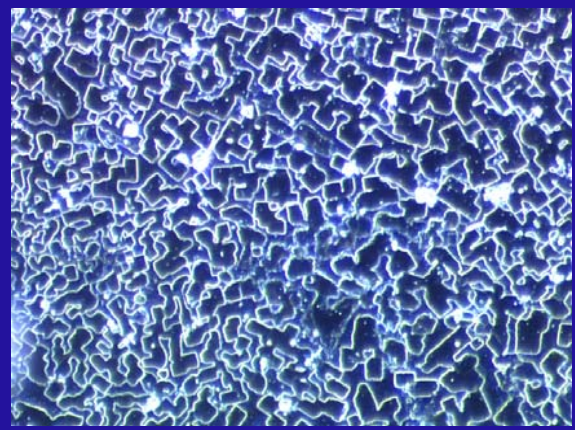


Fig. 1 (a) The structure and 'bowl-shape' of p-*tert*-butylcalix[5]arene. (b) The two types of TBC5 found in the toluene solvate and their respective 'near dimeric capsule' and 'partially overlapped dimer' arrangements observed upon symmetry expansion. The toluene guest molecules are shown in the centers of the TBC5 hosts. Note that the Type I and II arrangements of TBC5 are shown in orientations irrespective to one another within the actual crystal structure; these views are solely for visualization of the behavior of each independent calixarene from the asymmetric unit. (c) The 'self-including' chain found in the sublimed form of TBC5. Hydrogen atoms have been omitted and disordered *tert*-butyl groups of TBC5 molecules (in both structures) are only shown in one position for clarity in (b) and (c). Atom color code: Carbon = blue, Oxygen = red, Hydrogen = grey.

Gas Absorption/Desorption Measurement

- **Development of Quartz Crystal Microbalance (QCM) system crucial**
  - **CVD step**
    - **Purifies compound after bulk synthesis step**
    - **Stabilizes metastable phase with free cavities**
    - **Isolation from contact with atmosphere**
  - **Direct measurement of mass change**
    - **No buoyancy problems to address as with TGA**
    - **Highly sensitive technique (nanogram quantities)**





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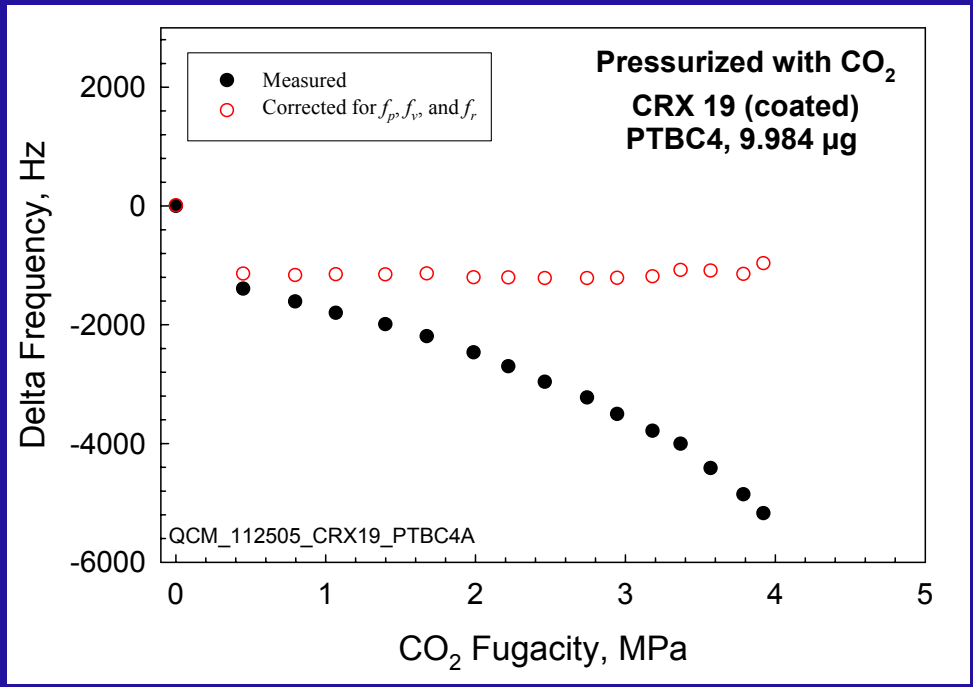
Surface Roughness Solution

Roughness Correction

$$\Delta f_r = -\frac{n f_o^2 \rho_g}{\pi(\rho_q \mu_q)^{-1/2}} \Phi$$

- Roughness coefficient Φ can be calculated because of physical limit on mass loading in clathrate
- Once roughness factor is known, it is applicable to other gas or gas mixtures



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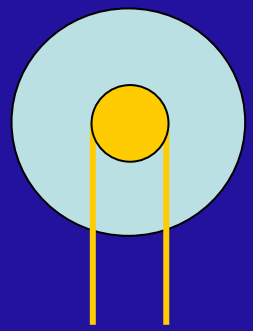
Issues with QCM Measurements

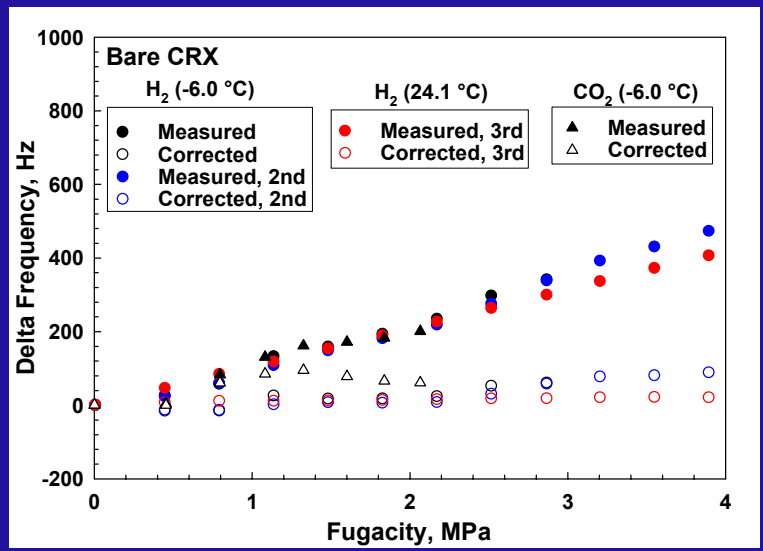
- Mass change is proportional to change in oscillator frequency but…
- Correction factors are required for:
  - Pressure (+)
  - Viscosity (-)
  - Surface Roughness (-)
  - Temperature (+)
    - Not significant between 0°C and 70°C but important outside these limits

Quartz Crystal Oscillator



Sauerbrey Equation

$$\Delta f = \frac{-2\Delta m}{A\sqrt{\mu_q \rho_q}} f_o^2$$



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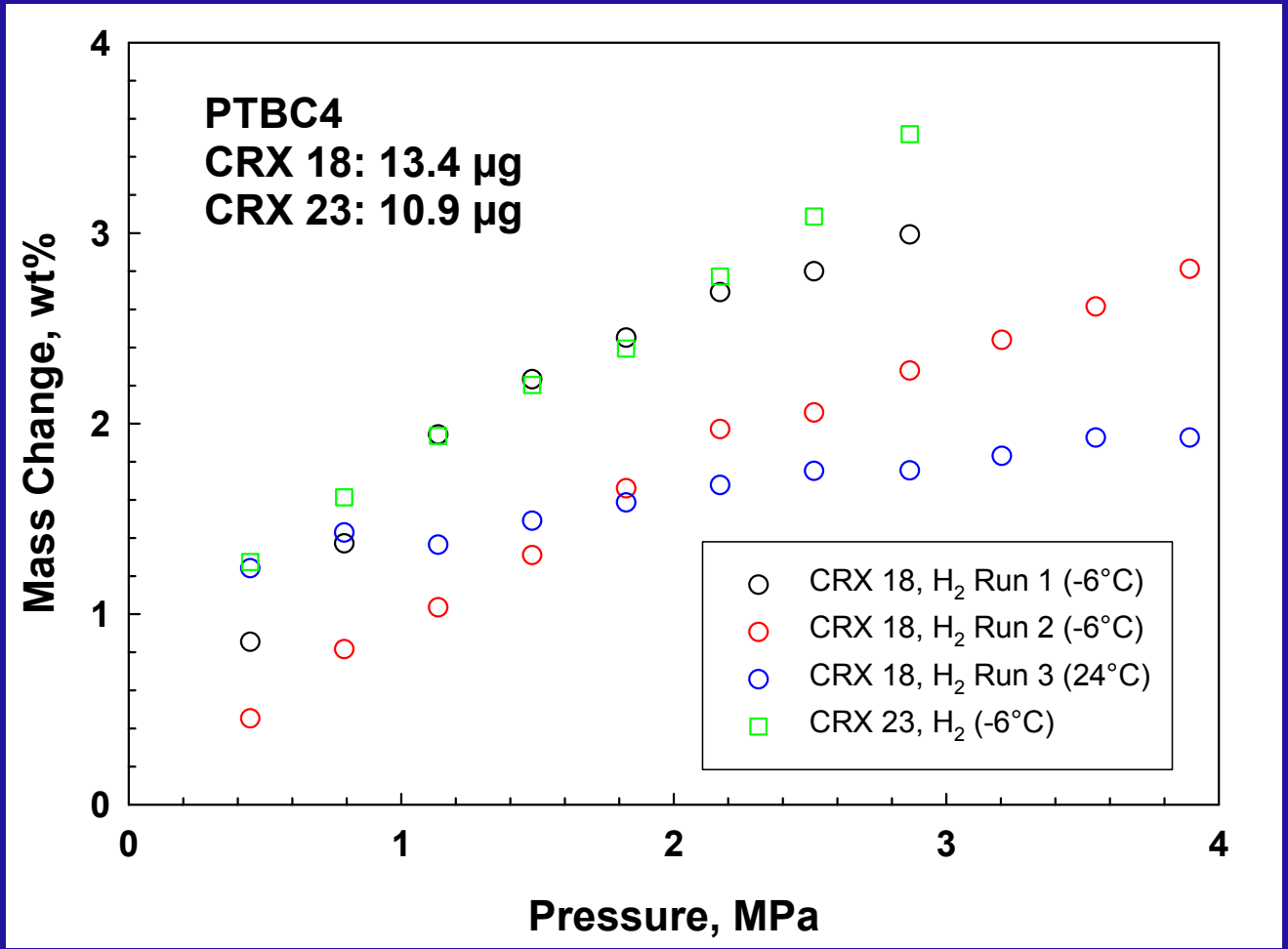
H_2 Uptake in PTBC4



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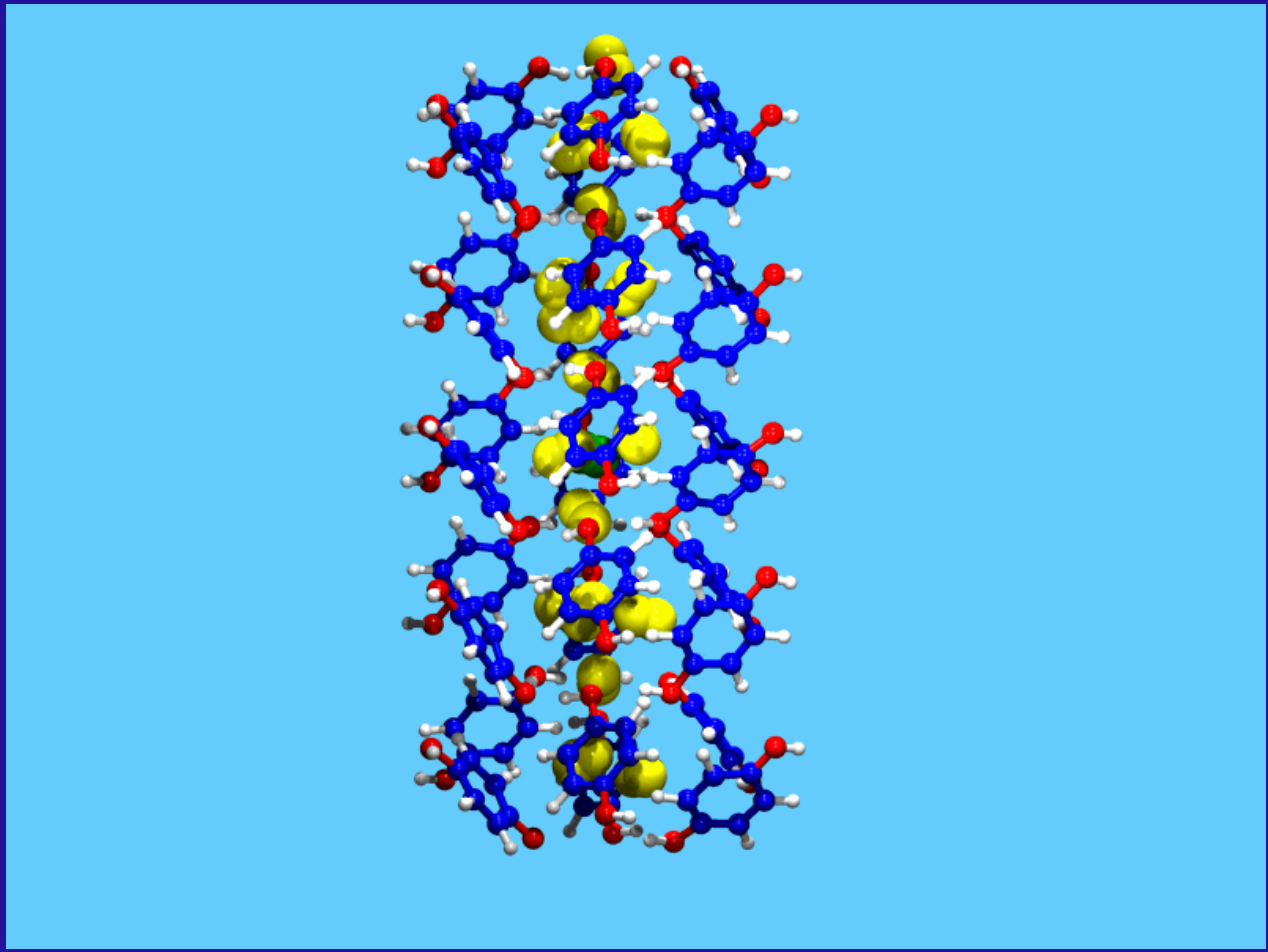
MD Simulation of Full 3-D Supercell



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